

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 23/10, 23/16, C08K 13/02, C08L 51/00, 51/04, H01B 3/44	A1	(11) International Publication Number: WO 99/27015 (43) International Publication Date: 3 June 1999 (03.06.99)
(21) International Application Number: PCT/IT97/00291 (22) International Filing Date: 21 November 1997 (21.11.97) (71) Applicant (for all designated States except US): COMMER S.P.A. [IT/IT]; Zona Industriale - Contrada Ficocelle, I-84061 Ogliastro Cilento (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): MASCIA, Francesco [IT/IT]; Via Cavour, 1, I-22070 Guanzate (IT). PUPPI, Cristiano [IT/IT]; Via Bellini, 28, I-22070 Guanzate (IT). (74) Agent: GISLON, Gabriele; Marietti e Gison S.r.l., Via Larga, 16, I-20122 Milano (IT).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: A PROCESS OF PRODUCING FIRE RESISTANT THERMOPLASTIC COMPOSITIONS AND COMPOSITIONS THUS OBTAINED (57) Abstract A halogen-free and fire resistant thermoplastic composition is produced by preparing a blend comprising a halogen-free thermoplastic material containing both, cross-linkable and non-cross-linkable compounds, a fire resistant inorganic filler, a compatibilizing agent for said inorganic filler, and a radical generating agent; the blend is mixed and dynamically cured at a temperature above the decomposition temperature of said radical generating agent to obtain a partially cross-linked thermoplastic composition and a grafting of the compatibilizing agent on all the bulk of thermoplastic material.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

**A PROCESS OF PRODUCING FIRE RESISTANT THERMOPLASTIC COMPOSITIONS
AND COMPOSITIONS THUS OBTAINED**

FIELD OF THE INVENTION

The present invention relates to a process of producing fire
5 resistant thermoplastic based materials, to the polymer
compositions thus obtained and to the products using said
compositions.

In more detail, the invention relates to halogen-free
thermoplastic materials that, filled with a high level of
10 inorganic compounds, grafted in bulk with compatibilizing
substances and dinamically "cured" with free radical generator
catalysts, are both fire resistant and provided with
surprisingly high thermomechanical properties.

BACKGROUND OF THE INVENTION

15 Halogen-free thermoplastic materials have a broad and useful
range of mechanical properties. Among them, polyolefins are a
chemically homogeneous class of polymers with a wide spectrum of
properties and a low level of environmental impact, so their use
is growing with an impressive rate and new materials, obtained
20 from new catalytic systems, came into the market offering new
applications.

These polymers, that contain mainly carbon and hydrogen, can
burn and propagate the flame very easily and there has been a
constant search for a way of removing this characteristic
25 without compromising their mechanical properties and without
transforming them in thermoset materials.

The higher the mechanical properties the larger the application
field for these materials. With hard and stiff materials
structural parts can be obtained like boxes, pipes, profiles,
30 panels; elastic and flexible materials can be used for covering
walls, wires or other objects for automotive, furnishing,
building or electrical industries in which fire resistance
without toxic substances emission in case of fire is requested.

A first, known, solution is to use inorganic compounds, i.e.

metal hydroxides (e.g. Mg and Al hydroxides), oxides and/or inorganic salts, having endothermic decomposition and releasing nonflammable gas (like water or carbon dioxide), and/or creating a protective shield when heated, as fillers in plastics or elastomers to impart flame retarding properties to said materials.

The flame retarding action of these inorganic compounds is based on physical reasons. Their endothermic thermal decomposition process subtracts heat to the burning bulk, reducing the release of flammable pyrolytic gases, and further diluting it with non flammable gas released by the inorganic compounds. In addition some of them can create a protective layer that acts as a shield against the flame propagation.

The main drawback of these inorganic fillers is that their effectiveness is pretty low and a high amount of filler is required to impart the polymer effective fire retarding properties (particular with resins, like polyolefins, that can burn completely). In fact, the required amount of filler is so high that the mechanical properties of the final material are dramatically jeopardized. By selecting the most endothermic and gas releasing compounds, such as light metal hydroxides (aluminium or magnesium hydroxides) or boron containing compounds, or by using them in combination with other flame retardant compounds - which interfere in the combustion chemistry - a slight reduction in the amount of filler was obtained. However, the required amount of filler is still so high that the mechanical properties of the final composition are pretty poor.

In order to overcome these problems it was suggested to improve the adhesion between the filler and the polymer by adding compatibilizing agents that should have affinity to the polymer and the filler as well. As a matter of fact it is known that the mechanical properties of blends between polyolefins and metal hydroxides are improved when a moderate amount of a polyolefin containing succinic units, vinylsilane, or other polar groups,

as side substituents, are added, because its olefinic part remains into the bulk of the polymeric part and the succinic residue bonds to the filler either chemically (salification of the hydroxide) or by means of electrostatic interaction.

- 5 Alternatively, it was suggested to add to the polymer matrix compounds like peroxides, grafted silanes or sulphur that after the final product is obtained in its final shape, in a dedicated step can crosslink ("cure") the polymer matrix of the final product. By this process the mechanical properties of the
10 polymer are improved but the polymer is transformed into a thermoset material that can not be further processed or recycled. This method is used for example for the production of cables, pipes, tyres, foamed sheets, etc.

OBJECT OF THE INVENTION

- 15 The aim of the present invention is to improve the mechanical properties of halogen-free fire resistant thermoplastic materials in which the fire resistance is given by an inorganic filler, by means of a chemical modification of the polymeric matrix during the blend with the filler, and to substantially
20 maintain the thermoplastic characteristics of the starting materials in the final composition.

SUMMARY OF THE INVENTION

- The invention relates to a reactive process to prepare halogen-free thermoplastic compositions having fire resistance
25 characteristics, according to claim 1.

- According to a preferred aspect of the invention, the inorganic filler is selected from $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, CaCO_3 , boric acid, borates, CaO , silica and mixtures thereof; the radical
30 generating agent is a peroxide and the compatibilizing agent is selected from maleic and fumaric acids, maleic and fumaric anhydrides and mixtures thereof.

- This invention also concerns halogen-free, fire resistant thermoplastic compositions as obtainable according to the claimed process, wherein compatibilizing agents are grafted over
35 all the bulk of said thermoplastic material. The final

composition is thermoplastic and is partially crosslinked.

The invention also relates to electric cables provided with a layer made with a fire resistant thermoplastic material according to the invention. Preferably, such layer is a shield.

- 5 The invention also relates to the use of a composition as above disclosed for the production of electric appliances and their parts, such as boxes, pipes, etc.

The invention provides several advantageous features.

- As above mentioned, the invention process results in a final
10 composition that is thermoplastic, i.e. it is further processable and recyclable. There thus is no need to give the product its final shape before curing it by heating the mixture and activating the peroxides; in fact a preferred shape for the invention composition is as pellets.

- 15 The invention compositions have surprisingly good properties, namely higher values of mechanical modulus, stress strain and elongation at break, impact behaviour, abrasion resistance, compression set and softening or distortion temperature, with respect to the properties of corresponding materials made
20 according to known techniques.

- These materials can be employed to obtain structural parts or to coat other objects to impart them the required characteristics of fire resistance features. They are processable by conventional processing technologies as: injection and
25 coinjection molding, extrusion, co-extrusion, blow-molding, roto-molding, slush molding, thermoforming.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

- According to the present invention the thermoplastic material useful for carrying out the process are selected from alpha-
30 olefines homo and co-polymers such as ethylene, propylene, ethylene/propylene, propylene copolymers containing one or more alpha olefins with 2-10 carbon atoms (e.g. ethylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene); EPM (ethylene/propylene) rubbers and EPDM (ethylene/propylene/diene)
35 rubbers; natural rubber; EVA (ethylene/vinylacetate);

ethylene/1-octene copolymer; polyenes homo and co-polymers such as polybutadiene; styrol/butadiene rubbers (SBR), hydrogenated styrol/butadiene copolymers; acrylonitrile/butadiene/styrene copolymer, their functionalized polymers; and mixtures
5 thereof. The starting thermoplastic material must contain both crosslinkable and non-crosslinkable compounds. The amount of thermoplastic material is usually about 5-70 wt.%, in any case it is such as to bring to 100 the composition.

The inorganic fillers imparting fire resistance are those
10 inorganic fillers that endothermically decompose with release of non-flammable gas and inert ashes. Examples of these fillers are aluminium trihydroxide, magnesium hydroxide, huntite $[3\text{MgCO}_3 \times \text{CaCO}_3]$ or hydromagnesite $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \times 4\text{H}_2\text{O}]$, boric acid. Other suitable fillers are those that can vetrify like
15 borate or hydrate borate, sodium bicarbonate, calcium oxide and silica. The fillers can be mixed together or diluted with inert materials like silica, or materials that decompose at higher temperatures than the polymer decomposition temperature, like calcium carbonate. Their total amount is within the range of 30-
20 80 wt.%, typically from 40% to 75% by weight of the final blend. The compatibilizers are molecules with chemical affinity to the filler, and able to graft, with a chemical bond, the macromolecular backbone by means of a free radical catalyzed reaction. Typically these compatibilizers are unsaturated
25 organic acids or esters, like acrylic, methacrylic, fumaric, maleic, citraconic or itaconic acid and esters, used in a concentration ranging between 0,005 and 10% by weight of the blend. Preferred compatibilizers are maleic and fumaric acids, maleic anhydride and mixtures thereof. Another class of useful
30 compatibilizers are the maleinized polybutadienes or vinyl-methoxysilanes that can graft the macromolecular backbone accelerating and or promoting the crosslinking reaction, used in concentration till 15% of the total blend.

The preferred amount of compatibilizers is within the range of
35 0.01-15 wt.%.

The free radicals generator agentss are preferably organic peroxides like dicumil peroxide, 2,5-di(terbutylperoxi)-2,5-dimethylhexane, or other molecules with a strained bond that omolitically breaks upon temperature increase, like 2,3-
5 dimethyl-2,3-diphenyl-butane. These free radical generator agents start radical chain reactions that both graft the compatibilizer molecule onto the macromolecules but also "cure" the polymer by crosslinking. Preferably, radical generating agents are provided in an amount of 0.01-2.0 wt.% of active
10 material.

Besides the above mentioned compounds, usual additives known in the plastics field such as antioxidants and stabylizers, plasticizers, lubricants, slipping agents and process coadiuvators are provided for in the invention composition. The
15 type and amount of these additives are directly derivable from known formulations and are not object of this invention.

According to the invention the process of preparing a thermoplastic composition that is fire resistant, free from halogens and really thermoplastic (i.e. further processable or
20 recyclable) provides to prepare a blend comprising: a halogen-free thermoplastic material containing both crosslinkable and non-crosslinkable compounds, a fire resistant inorganic filler, a compatibilizing agent for said inorganic filler, and a radical generating agent, and to dinamically cure said blend to obtain a
25 partially crosslinked thermoplastic composition.

"Dinamically curing" the above blend or mixture means that the blend is melted and kneaded at a temperature above the decomposition temperature of said radical generating agent in order to start and carry out the reticulation of the
30 macromolecules, i.e. the crosslinking, or the degradation of the macromolecules, according to their nature. The action of the radical generating agents occurs in the presence of the filler and of the compatibilizer to obtain the required grafting

The macromolecular structure of the thermoplastic material is
35 modified in a way that depends from its initial structure and

composition: with polymers having unsaturated carbon-carbon bonds like ethylene/propylene/diene rubber or styrole/butadiene rubber, or having more than 50% (moles) of ethylenic units in the backbone like polyethylene, ethylene/1-octene (or 1-hexene) copolymers, ethylene/propylene rubber, ethylene/vinylacetate, hydrogenated styrole/butadiene rubber the main result of the radical chain reactions is a macromolecular crosslinking.

If the macromolecular structure has no unsaturated carbon-carbon bonds and more than 50% (moles) of substituted vinyl units ($\text{CH}_2\text{-CHR-}$, R different from H) like in polypropylene, the main radical reaction is a chain scission or degradation to give shorter chains.

This structural change control is a crucial point to improve the material characteristics that can be customized balancing the degradation and the crosslinking by accurate polymer and additives choice.

For hard and stiff materials, polymers like polypropylene, that is degraded by radical generators, without any crosslinking reaction, are frequently employed. The control of this degradation and some degree of crosslinking is possible by employing polymers rich in double bonds such as polybutadienes, polyalkenylenes, plyenes and EP(D)M rubbers that graft and join the macromolecules by free radical catalyzed reactions.

For flexible thermoplastic materials, a curable rubber is frequently employed but the complete crosslinking that should transform the polymer in a thermoset material is avoided by using some amount of polypropylene or other non-crosslinkable compound. The non-crosslinkable, degradable, compound substantially acts as a continuous phase in which the cured (or crosslinked) phase is dispersed.

The formulation of the composition, i.e. the amounts of degradable polymers, curable polymers, peroxide and polymers rich in double bonds, is balanced according to the mechanical characteristic that are required for the final product. If elastomeric properties are required, a greater amount of

crosslinkable compounds will be present in the initial thermoplastic material; if a rigid final product is required, the amount of degradable, non-crosslinkable (i.e. uncurable) compound will be greater than the amount of curable
5 (crosslinkable) compound.

The invention process provides to carry out the mixing, melting, kneading, compatibilizing and curing/degrading of the blend components substantially in one step. The inorganic filler is usually added immediately after the reaction is started on the
10 rest of the mixture, as disclosed by the following examples.

A preferred apparatus to carry out the process is an extruder, most preferably co-rotating twin screws extruders with a high dispersing and homogeneization capacity, good temperature control and high ratio L/D, where L is the barrel length and D
15 is the barrel diameter.

EXAMPLES

Several starting compounds in different amounts were processed according to the invention in a MARIS ® (Turin, Italy) TM 133 co-rotating twin screws extruder with L/D=40. The filler was
20 added at about 1/3 of the barrel length through a side feeder. Antioxidants, in any, were added at 2/3 of the barrel length. A vacuum device was used to remove moisture and volatile by-products. The processed material was cut into pellets, cooled in water and dried in a spin dryer.

The samples for assessing the mechanical characteristics of the final material were obtained by injection molding according to ASTM D638, this being further evidence that all of the invention compositions are thermoplastic materials. The mechanical characteristics are listed in table 1 (elastomeric composition)
30 and in table 2 (rigid compositions).

In table 1, examples 1, 5 and 6 are referring to state of the art processes. In 1 no peroxide or compatibilizing agent was used; in 5 and 6 the compatibilizing agent (comp¹) was previously grafted on a polymer matrix (polypropylene) and subsequently
35 added to the invention blend, the poor results are self evident,

also in ex.6 where a high amount of comp¹ was added.

Example 2 shows a comparative example in which peroxide only was used. Example 3 repeats the formulation of example 2, with the addition of maleic anhydride: the value of tension at break
5 increased from 16 to 20 MPa.

This is the legenda for examples 1-8.

- 1) comp is a compatibilizing agent "POLYBOND 3150" ® by Uniroyal Chemical
- 2) Dicumyl peroxide by Oxido
- 10 3) Polypropylene homopolymer Daplen DS10 by PCD
- 4) Ethylene/1-octene copolymer Engage 8150m by DuPont-Dow Elastomers
- 5) Ethylene/propylene copolymer C0059 by Enichem Elastomeri
- 6) ethylene/propylene copolymer Stamylan 56M10 by DSM
- 15 7) ethylene/propylene random copolymer Daplen CHC 3007 by PCD

In table 2 examples 9-10 refer to rigid compositions and show the surprising results of invention composition 11 with respect to comparative examples 9 and 10.

The added legenda references for table 2 are:

- 20 8) ASTM 1238 (230°C, 2.16)
- 9) ASTM D 256
- 10) polypropilene homopolymer: Valtec MH113Y by Himont
- 11) EPDM: Dutral Ter 4038 by Enichem Elastomeri

TABLE 1

Exmpl.	pp	elastomer	Mg(OH) ₂	CaCO ₃	MAh	comp ¹	perox. ²	tens at break	elong at break
	%	%	%	%	%	%	%	MPa	%
1	7.48 ³	29.79 ⁴	60.5	2.23	0	0	0	6.5	1075
2	7.48 ³	29.79 ⁴	60.5	2.18	0	0	0.05	16	225
3	7.48 ³	29.79 ⁴	60.5	2.00	0.18	0	0.05	20	210
4	7.48 ³	29.79 ⁴	60.5	1.96	0.18	0	0.09	23	198
5	6.00 ³	29.99 ⁵	60.5	2.00	0	1.51	0	8.3	730
6	6.00 ³	15.8 ⁵	60.5	2.00	0	15.7	0	14.1	130
7	7.48 ⁶	29.79 ⁴	60.5	2.00	0.18	0	0.05	17.5	227
8	7.48 ⁷	29.79 ⁴	60.5	2.00	0.18	0	0.05	19.4	218

TABLE 2

Exempl.	pp	elastomer	Mg(OH) ₂	CaCO ₃	MAh	comp ¹	perox ²	MFI ⁸	Flexural modulus	IZOD ⁹ Notched 23°C
	%	%	%	%	%	%	%	MPa	MPa	J/m
9	35 ¹⁰	0	62	3	0	0	0	10	3800	28
10	34.47 ¹⁰	0	62	3	0.5	0	0.03	12	3850	35
11	25 ¹⁰	9.45 ¹¹	42	23	0.5	0	0.03	6	2500	45

CLAIMS

1. A process for the preparation of a fire resistant thermoplastic composition, wherein a blend comprising a halogen-free thermoplastic material containing both crosslinkable and non-crosslinkable compounds, a fire resistant inorganic filler, a compatibilizing agent for said inorganic filler, and a radical generating agent, is mixed and dynamically cured at a temperature above the decomposition temperature of said radical generating agent to obtain a partially crosslinked thermoplastic composition.
2. A process according to claim 1, wherein said blend comprises 30-80 wt.% of said inorganic filler, 0.01-2.0 wt.% of active radical generating agent and 0.01-15 wt.% of compatibilizing agent.
3. A process according to claim 1 or 2, wherein said fire-resistant inorganic filler is selected from $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, CaCO_3 , boric acid, borates, CaO , silica, and mixtures thereof; said radical generating agent is a peroxide and said compatibilizing agent is selected from maleic and fumaric acids, maleic anhydride and mixtures thereof.
4. A process according to any previous claim, wherein said non-crosslinkable compound comprises a propylene polymer and said crosslinkable compound is a polyene and/or a rubber selected from EPM and EPDM rubbers, natural rubber, EVA, polyalkenylenes, ethylene/1-octene copolymer, styrol/butadiene rubbers (SBR), hydrogenated styrol/butadiene copolymers, acrylonitrile-butadiene-styrene copolymer, their functionalized polymers, and mixtures thereof.
5. A process according to claim 4, wherein said rubber is oil extended and said thermoplastic material comprises a polymer rich in double bonds such as polybutadiene.
6. A process according to any previous claim, wherein a first blend is prepared, melted and kneaded to decompose said radical generating agent, said fire-resistant inorganic filler is added to said blend and heating and kneading of the complete blend is

continued to obtain said partially crosslinked thermoplastic composition.

7. A thermoplastic, fire resistant composition as obtainable according to the process of any claim 1 to 6, comprising a
5 halogen-free thermoplastic material containing both a crosslinked and non-crosslinked portion, a fire resistant inorganic filler, a compatibilizing agent for said inorganic filler, said compatibilizing agent being grafted over all the bulk of said thermoplastic material.
- 10 8. A composition according to claim 7, in the form of pellets.
9. An electric cable, characterized in comprising a layer made of a composition according to claim 7.
10. The use of a composition according to claim 7 for the manufacture of fire resistant portions of electric appliances.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IT 97/00291

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L23/10 C08L23/16 C08K13/02 C08L51/00 C08L51/04
H01B3/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C08K H01B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 269 274 A (MITSUI PETROCHEMICAL IND) 1 June 1988 see examples 18-39	1,2,4,7
Y	---	1-4,7-10
X	EP 0 614 940 A (MITSUI PETROCHEMICAL IND) 14 September 1994 see examples E38,,E48-E72	1,2,4,7
Y	---	1-4,7-10
Y	EP 0 237 713 A (SUMITOMO BAKELITE CO) 23 September 1987 see page 3, line 13-23 see page 26, line 27 - page 27, line 5	1-4,7-10
E	EP 0 822 223 A (COMMER SPA) 4 February 1998 see tab. 1, ex. 7, tab. 2, ex. 5,6 --- -/-	1,4,7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

21 July 1998

Date of mailing of the international search report

14.08.98

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Voigtländer, R

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/IT 97/00291

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 280 761 A (SUMITOMO BAKELITE CO) 7 September 1988 see claim 1; example 1 ---	1,7
A	EP 0 462 680 A (MITSUI PETROCHEMICAL IND ;SHELL OIL CO (US)) 27 December 1991 see claim 1; example 1 ---	1,7
A	EP 0 370 517 A (NIPPON UNICAR CO LTD) 30 May 1990 see page 3, line 21-33; examples 1-16 ---	1,7
A	EP 0 370 518 A (NIPPON UNICAR CO LTD) 30 May 1990 see claim 1 ---	1,7
A	EP 0 546 841 A (NIPPON PETROCHEMICALS CO LTD) 16 June 1993 see claims 1,9,17,18,20; example 72 ---	1,7
A	KEONELLI, E. ET AL.: "Non-halogenated, flame retardant ..." KAUTSCHUK + GUMMI KUNSTSTOFFE, vol. 44, no. 10, 1991, page 960-962 XP002072157 see the whole document -----	1,7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IT 97/00291

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 6
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
IT IS UNCLEAR WHICH COMPONENTS A "FIRST BLEND" HAS TO COMPRISE. CONSEQUENTLY SUCH A CLAIM IS NOT SEARCHABLE.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IT 97/00291

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0269274 A	01-06-1988	AU 600984 B	30-08-1990
		AU 8047987 A	05-05-1988
		CA 1335911 A	13-06-1995
		CN 1023705 B	09-02-1994
		DE 3788506 D	27-01-1994
		DE 3788506 T	14-04-1994
		JP 1927155 C	25-04-1995
		JP 6049813 B	29-06-1994
		JP 63270754 A	08-11-1988
		US 5310800 A	10-05-1994
EP 0614940 A	14-09-1994	JP 1259048 A	16-10-1989
		JP 1259047 A	16-10-1989
		JP 1259049 A	16-10-1989
		JP 2585699 B	26-02-1997
		JP 1295846 A	29-11-1989
		JP 2595302 B	02-04-1997
		AT 124965 T	15-07-1995
		AU 3255789 A	12-10-1989
		CA 1339286 A	12-08-1997
		DE 68923392 D	17-08-1995
		DE 68923392 T	21-12-1995
		EP 0336780 A	11-10-1989
		KR 9704919 B	08-04-1997
		US 5247018 A	21-09-1993
EP 0237713 A	23-09-1987	JP 62181353 A	08-08-1987
		JP 62285943 A	11-12-1987
		AU 577971 B	06-10-1988
		AU 6712987 A	06-08-1987
		CA 1275520 A	23-10-1990
		DE 3785378 A	19-05-1993
		NO 176719 B	06-02-1995
		US 4732939 A	22-03-1988
		FI 871807 A,B,	25-10-1988
EP 0822223 A	04-02-1998	NONE	
EP 0280761 A	07-09-1988	AU 578184 B	13-10-1988
		AU 7539487 A	01-09-1988

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IT 97/00291

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0280761 A		CA 1275521 A	23-10-1990
		DE 3784486 A	08-04-1993
		FI 873150 A,B,	03-09-1988
		JP 1983681 C	25-10-1995
		JP 2196839 A	03-08-1990
		JP 7010941 B	08-02-1995
		NO 176967 B	20-03-1995
		US 4801639 A	31-01-1989
EP 0462680 A	27-12-1991	JP 1920520 C	07-04-1995
		JP 6049814 B	29-06-1994
		JP 61213248 A	22-09-1986
		JP 1945403 C	23-06-1995
		JP 6080156 B	12-10-1994
		JP 61213249 A	22-09-1986
		AT 143990 T	15-10-1996
		AU 581974 B	09-03-1989
		AU 5478786 A	25-09-1986
		CA 1266736 A	13-03-1990
		DE 3650576 D	14-11-1996
		DE 3650576 T	20-03-1997
		DE 3688568 A	22-07-1993
		EP 0201996 A	20-11-1986
		US H568 H	03-01-1989
EP 0370517 A	30-05-1990	JP 2145632 A	05-06-1990
		JP 2753840 B	20-05-1998
		AT 120473 T	15-04-1995
		DE 68921959 D	04-05-1995
		DE 68921959 T	27-07-1995
EP 0370518 A	30-05-1990	JP 2145633 A	05-06-1990
EP 0546841 A	16-06-1993	CA 2084491 A	11-06-1993
		CN 1074454 A	21-07-1993
		DE 69224712 D	16-04-1998
		DE 69224712 T	02-07-1998
		JP 5239281 A	17-09-1993
		JP 5247278 A	24-09-1993
		US 5418272 A	23-05-1995

Information on patent family members

PCT/IT 97/00291

Form PCT/ISA/210 (patent family annex) (July 1992)